

# Effects of gating and contact geometry on current through conjugated molecules covalently bonded to electrodes

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We study the effects of gating and contact geometry on current through self-assembled monolayers of conjugated molecules strongly coupled to gold electrodes by sulfur “anchor groups”. The current changes by more than an order of magnitude depending on the angle between the axis of the benzenedithiolate molecules and the normal to the electrode on the less coordinated “top site” position. The effect of gating is also much stronger in this case compared to higher coordinated “hollow site” binding of the molecule on a Au(111) surface. The large hybridization of the molecular states with electrode states for the hollow site leads to practically ohmic current-voltage characteristics. Changes in molecule-electrode geometry accompanying the gating of the SAM may be the reason for strong changes of the conductance observed by Schön *et al.* in the “slot” geometry.

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## I. INTRODUCTION

Studies of electron transport through organic molecules (molecular films), viewed as the possible components of molecular electronic devices, are a very active area of research [1–3]. Although the rectifying properties of the molecules in two-terminal devices were demonstrated in 1990s [4], only recently have *three*-terminal devices based on a self-assembled monolayer (SAM) of simple conjugated molecules containing either one or two phenyl rings  $C_6H_6$  or two or three thiophen rings  $C_4H_4S$  been fabricated [5]. The molecules were gated from the edge of the vertical device through  $L = 30$  nm of  $SiO_2$  gate oxide (30 nm was the nominal oxide thickness, but the high-resolution transmission electron microscopy showed much thinner oxide barrier of 4–5 nm [7]). In the slot geometry of this experiment, the drain current  $I_d$  through only several thousand molecules close to the gate oxide should have been affected by the gate voltage  $V_g$ . The measured conductance  $dI_d/dV$  at zero source-drain bias was about 5  $\mu S$ /molecule. The gating field on the molecules should be small because the length of the molecules (the “channel” length) is tiny,  $2t = 1 - 2$  nm, so that the geometrical aperture factor is small,  $t/L \ll 1$ . In spite of this, Schön *et al.* have initially estimated a dramatic change of conductance of the molecules by a factor to be about  $10^7$  (it was later determined that the effect was overestimated, probably because of disorder and other factors in pure SAMs [7]), with a large transconductance  $dI_d/dV_g = 12 - 13$  mA/V for pure SAMs of biphenyl molecules and about 6 mA/V for phenyls [5] at room temperature. Dilute systems of conducting molecules (namely, 4,4'-biphenyldithiol and some other species) embedded in a matrix of non-conducting alkanedithiols have

also been measured with the aim to sample individual conducting molecules [6]. Schön *et al.* have found that the conductance through the molecule is about  $0.1 \mu A/V$  at zero drain voltage  $V = 0$ , and approaches one conductance quantum  $2e^2/h = 77.5 \mu A/V$  at relatively small gate voltage  $V_g \approx -0.3$  V. The histograms of conductance measured on a series of devices suggested that the conductance through the gated molecules was quantized in the fundamental units of  $2e^2/h$ . The conductance peak position varied with the gate voltage  $V_g$  from device to device. The transconductance  $dI_d/dV_g$  was found to be in the range of  $150 \mu A/V$  at 4K, *decreasing* to about  $10 \mu A/V$  at room temperature (in the earlier measurements the peak value of  $dI_d/dV_g$  was estimated of about 13 mA/V [5] for the biphenyl molecules). The corresponding modulation of conductance in the film of individual dithiol molecules has been estimated to be much larger than  $10^3$ . This is a huge effect indeed if it is to be explained by a mechanism related to the behavior of individual molecules.

Very recently this work has been extended to SAMs of benzene-(1,4)-dithiolate ( $-S-C_6H_4-S-$ ), the simplest conjugated molecules, referred to below as BDT, with only one phenyl ring [7]. The area of the measured device comprised about  $10^4$  molecules, mostly non-conducting alkanes with a small fraction ( $10^{-4}$ ) of the conducting BDT molecules [7]. In this geometry, only one or a few BDT molecules should have contributed to transport. The first peak in BDT conductance has been found at a bias of about 2.1V with the corresponding value of  $25 \mu A/V$  [7]. Interestingly, the conductance appeared to be much larger than that found in the earlier break-junction experiments by Reed *et al.* [8] who observed the first peak in conductance of  $0.05 \mu A/V$  at 1.4V. Schön and Bao have also observed a jump in conductance from 0.7–1.0  $\mu A/V$

to much larger values close to the conductance quantum  $77.5 \mu\text{A/V}$  at the gate voltage  $V_g \approx -0.4 \text{ V}$  and the drain voltage of about  $-0.7 \text{ V}$  (this is a jump of almost two orders of magnitude). The position of this switching shows some *hysteresis* when the gate voltage is varied in the range  $-0.6 < V_g < 0 \text{ V}$ . This hysteretic behavior cannot possibly come from the individual molecule behavior and should be related to some *extrinsic* mechanism, as we shall discuss below. Also interesting is the observed change in the fine structure of the conductance: there is a series of small peaks  $45 \text{ meV}$  apart from each other on the conductance curve for  $V_g = 0$ , and the period shrinks down to  $40 \text{ meV}$  at  $V_g = -0.5 \text{ V}$ . Such peaks are usually attributed to tunneling assisted by molecular vibronic excitations, so the change in the period indicates a possible change in molecular conformation. These abrupt changes cannot be explained by the electric field created by the gate, since the corresponding field on the molecule should be small.

With regards to a possible origin of the observed behavior, we first mention the importance of the geometry of the molecule-electrode contact [9]. If the orientation of the molecule with respect to an electrode changes, so does its conductance. Indeed, we have found earlier that the conductance of BDT (or any other conjugated thiol-terminated molecule) strongly depends on the angle  $\theta$  between the molecular “backbone” and the normal to the gold surface (Fig. 1). In a simple “toy” model, the current dependence is  $\propto \sin^2 \theta$  in the regime of strong resonant tunneling (large bias) and even stronger,  $\propto \sin^4 \theta$  in the regime of non-resonant tunneling (small bias) [9]. Note that the angular dependence of current is much stronger when the end sulfur is in the less-coordinated “top-site” position above a surface Au atom, compared to a “hollow-site” position, when it is bonded to three surface gold atoms, see Fig. 1. These bonding positions were considered in the literature as being the most favorable [10]. Indeed, it has been provisionally suggested that the conformational changes of the BDT with respect to electrodes, discussed in [9], are responsible for the observed “switching” behavior of SAMFETs [7]. Also, one cannot exclude that the observed changes in conductance through BDT are caused by charge trapping-detrapping processes close to the interface between the molecular layer and the gate  $\text{SiO}_2$ .

## II. SELF-CONSISTENT CALCULATIONS OF ELECTRONIC STRUCTURE AND TRANSPORT

In order to gain more insight into the origin of the observed extraordinary dependence of molecular conductance on a weak gating field observed in Refs. [7,6], we have performed a series of self-consistent calculations for different attachments of the BDT molecule to Au(111) surface. We have found that the effects of charge redis-

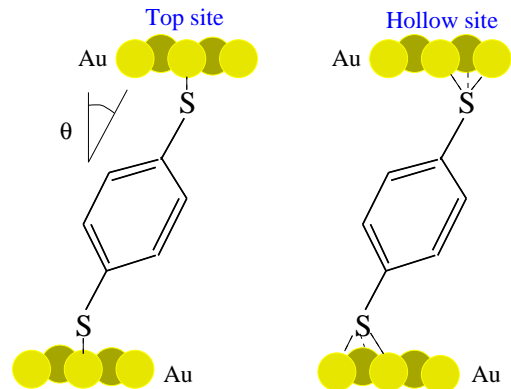


FIG. 1. Schematic of the benzene-dithiolate molecule on top and hollow sites. End sulfur atoms are bonded to one and three surface gold atoms, respectively.  $\theta$  is the tilting angle.

tribution as a function of molecular configuration and/or external field are important, since the mismatch between the work functions of Au and BDT results in a considerable charge flow between the molecule and gold electrodes. Without external bias, the lowest unoccupied molecular orbital (LUMO) lies closer to the Fermi level of Au compared to the highest occupied molecular orbital (HOMO). The current through the molecule strongly depends on both the tilting angle and the self-consistent charge redistribution across the molecule. Although it is not clear *a priori* what the sign of the combined effect would be, we have found that our previous conclusion about strong orientation dependence of the conductance through anisotropic conjugated  $\pi$ -orbitals and the  $s$ -orbitals on electrode Au remains valid [9].

BDT attaches strongly to the gold substrate by thiolate end groups  $-\text{S}-$  that form covalent bonds with Au [8,11]. In order to properly account for such a bonding in the present calculations, the Au atom(s) connected to S are treated separately from other gold atoms that compose the gold electrode. The conductance is computed with the use of the general procedure of Ref. [12]. The gold electrodes are described by a tight binding model with nine  $s$ -,  $p$ -, and  $d$ -orbitals per each Au atom with parameters from Ref. [13]. The equilibrium molecular geometry is found by total-energy density functional minimization [14]. The tight-binding parameters for the molecules and molecule-lead interfaces are taken from the solid-state table of elements [15].

The onsite energies in the present tight-binding model, which are very important for finding the correct charge redistribution between the molecule and the electrodes, have been estimated from the Hubbard model in the atomic limit. The energy of an isolated atom is approximated as  $E_m = E_0 - \epsilon \Delta q_m + \frac{1}{2} U \Delta q_m^2$ . Here  $E_0$  is the energy of a neutral atom with the atomic energy level at  $-\epsilon < 0$  with respect to the vacuum level (energy origin),  $\Delta q$  is the excess charge of an atom, and  $U$  is the intraatomic Coulomb repulsion. In this approximation, we

obtain  $\epsilon = \frac{1}{2}(A + I)$ ,  $U = I - A$ , where  $A$  and  $I$  are the experimental atomic values for the affinity and the ionization energy, respectively. These expressions have been used to estimate the following parameters used in the present work:  $U = 11.5$ ,  $\epsilon = 7.8$  for H;  $U = 6.3$ ,  $\epsilon = 5.2$  for C;  $U = 7.8$ ,  $\epsilon = 6.5$  for S; and  $U = 6.7$ ,  $\epsilon = 5.9$  for Au (all in units of eV). We would like to mention that the use of different values for the one-electron energies  $\epsilon$ , like the ones from Ref. [15]) leads to unphysically large charge transfers.

We have calculated the current through BDT on Au(111) in both the top-site and the hollow-site positions. Including onsite and intersite Coulomb interactions one finds that the onsite one-electron energies for state  $a$  at the site  $m$  should be adjusted as

$$\epsilon_{ma} = \epsilon_{ma}^0 + U_m \Delta q_m + \sum_{m'(m' \neq m)} e \gamma_{mm'} \Delta q_{m'} + e \phi_m^I, \quad (1)$$

where  $\epsilon_{ma}^0$  are the onsite energies in a system with neutral atoms,  $\Delta q_m$  are the charges on sites,  $\gamma_{mm'} = 1/|\mathbf{m} - \mathbf{m}'|$ ,  $\phi_m^I$  the image potential, and  $e < 0$  is the electron charge [16]. The charge  $\Delta q_m$  is found self-consistently from the local density of states, which is given by the site-projected imaginary part of the exact Green's function of the problem. The total retarded Green's function  $G_{mam'a'}(E)$  is calculated by “attaching” the semi-infinite leads to the molecule [12]. As a result of the attachment the molecular levels acquire a width that strongly depends on the coupling between electrode and the molecule,  $\Gamma \sim t_{\text{Au-S}}^2/D_{\text{Au}}$ . Here  $D_{\text{Au}}$  is the width of the s-band for Au electrodes,  $t_{\text{Au-S}}$  is determined mainly by the  $sp\sigma$  hopping integral from Au to the end sulfur atom on the BDT molecule, which is of the order of 1-2 eV. One should expect significant broadening of the molecular levels when the molecule is attached by a thiol group to Au, since a strong chemical bond is formed.

Under *zero* bias voltage, the electron charge  $q_m$  on the site  $m$  can be found from the Green's function in the standard manner as

$$q_m = \sum_a \int_{-\infty}^{\infty} dE N_{ma}(E) f(E), \quad (2)$$

$$N_{ma}(E) = -\frac{1}{\pi} \text{Im} G_{mama}(E), \quad (3)$$

where  $N_{ma}(E)$  is the density of states  $a$  on the site  $m$ ,  $f(E) = (1 + \exp \frac{E - E_F}{T})^{-1}$  is the Fermi function, and  $E_F$  is the chemical potential found from the global charge neutrality of the system.

In the case of finite bias voltage the system is out of equilibrium and one has to find the charge that is “flowing-in” from the electrodes onto the molecule, cf. [16]. Then the DOS on the site  $m$ , related to the influx of electrons from the lead  $w = 1, 2, \dots$ , is written as  $N_m^w(E) =$

$$2(\text{for spin}) \sum_{k_z^w, \mathbf{k}_{||}^w} \left| \psi_m(k_z^w, \mathbf{k}_{||}^w) \right|^2 \delta(E - E_{k_z^w, \mathbf{k}_{||}^w}^w),$$

where  $\psi_m^w(k_z, \mathbf{k}_{||})$  is the wave function at the molecular site  $m$ , which asymptotically becomes an incident Bloch wave in the lead  $w$  far from the molecule with the wave vectors  $(k_z, \mathbf{k}_{||})$ . Now we can find the occupation number for that site on the molecule due to charge flowing in from the lead  $w$  as  $q_m = \sum_w \int_{-\infty}^{\infty} dE N_m^w(E) f_w(E)$ , where  $f_w(E)$  is the Fermi function for the  $w$ th lead (i.e. with  $E_F = E_{Fw}$ ). In order to calculate the Green's function (and the charges  $q_m$ ) we define the “channels” such that  $k_z = k_z^w(E)$ , where  $l = 1, M$  enumerates all the quantum states in the lead unit cell (slice) [12]. It is convenient to re-write the expression for the charges in terms of “open channels”. The “open channel” is defined as a Bloch wave which propagates in the lead at a given energy. The Bloch waves incident on the molecule (i.e. having the velocities towards the scatterer,  $v_l > 0$ ) will contribute to the charge flowing to the molecule from a particular lead:

$$\begin{aligned} N_m^w(E) &= 2 \sum_{\mathbf{k}_{||}^w} \frac{1}{2\pi} \int_{-\pi/d_z}^{\pi/d_z} dk_z^w \left| \psi_m(k_z^w, \mathbf{k}_{||}^w) \right|^2 \delta(E - E_{k_z^w, \mathbf{k}_{||}^w}^w) \\ &= 2 \frac{1}{2\pi} \sum_{\mathbf{k}_{||}^w} \sum_{l(v_l^w > 0)} \frac{1}{\hbar v_l^w} \left| \psi_m^w(k_{zl}, \mathbf{k}_{||}) \right|^2, \end{aligned} \quad (4)$$

where  $d_z$  is the unit cell length along the lead.  $\psi_m^w$  are normalized for the length of the wire, which drops out of the final answers. Note that the integration in (4) goes over the *whole* Brillouin zone, not just over  $k_z > 0$ . The delta-function picks up the open channels on the leads. From now on we can drop the lead index and assume that one can later sum up all the charges flowing from all the leads. Once the Hamiltonian is set up, one calculates the charges on the sites, recalculates the onsite energies  $\epsilon_{ma}$  and continues iteratively until the charges converge.

The current through the film is given by a standard expression [17,12]

$$I = \frac{2q}{h} \int dE \left[ f\left(E - \frac{qV}{2}\right) - f\left(E + \frac{qV}{2}\right) \right] T(E), \quad (5)$$

where  $q = |e|$  is the elementary charge, and  $T(E)$  is the transmission probability

$$T(E) \equiv \sum_{\mathbf{k}_{||}, nn'} |t_{nn'}(E, \mathbf{k}_{||})|^2, \quad (6)$$

where the summation goes over the surface Brillouin zone of the lead. Transmission coefficients  $t_{nn'}(E, \mathbf{k}_{||})$  between the scattering channels  $n$  and  $n'$  are found from the solution of the scattering problem [12]. In the case of weak molecule-electrode bonding the transmission probability is approximately given by the Breit-Wigner formula [9]

$$T(E) \approx \sum_r \frac{\Gamma_{rL} \Gamma_{rR}}{(E - E_r)^2 + (\Gamma_{rL} + \Gamma_{rR})^2/4}, \quad (7)$$

where  $E_r$  enumerates the energies of the molecular orbitals (MOs) contributing to transport (not all of them do, see Figs. 2, 3),  $\Gamma_{rL(R)}/\hbar$  is the rate of the carrier transfer to the left (right) electrode from the molecular orbital  $r$ . This formula applies when the width of the MOs is much smaller than the energy difference between them, so that the resonances do not overlap. Each conducting molecular orbital produces a step-like contribution to the current. Indeed, when the resonance falls into the “window” between the lowest and the highest Fermi levels in the leads  $E_{FL} < E_r < E_{FR}$ , the current obtained from Eq. 5 is

$$I \approx \frac{2q}{\hbar} \frac{\Gamma_{rL}\Gamma_{rR}}{\Gamma_{rL} + \Gamma_{rR}}. \quad (8)$$

It follows from this analysis that the current-voltage characteristic should look as a series of steps, occurring when the resonant conditions are satisfied for particular conducting molecular orbital. The apparent negative differential resistance (NDR) at bias above 2V, Figs. 4-6, results not from resonant tunneling but from the electrode density of states. In the present model the electrode DOS is bounded from above for each particular value of  $\mathbf{k}_{\parallel}$ . As a result, the current will be zero at the energies above some threshold. The apparent NDR persists in the present calculations irrespectively of the number of basis functions (s-, sp-, or spd-basis), Fig. 6.

### III. EFFECTS OF CONTACT GEOMETRY AND GATING ON CURRENT-VOLTAGE CHARACTERISTICS

We argue below that gating of SAMs in the experiments [7,21] may have led to changes in molecule-electrode geometry and, consequently, to large changes in conductance. Given the strong orientational dependence of the current through conjugated molecules like BDT, and that in experimental SAMs the molecules are never positioned strictly normal to the electrode surface (as was assumed in Refs. [18,19]), we shall present the results for the transmission, density of states (Figs. 2, 3) and I-V curves (Figs. 4-6) for a series of tilting angles  $\theta$  between the backbone of the molecule and the normal to the Au(111) surface. The  $\theta$ -dependence of the I-V curves for BDT on the top site and hollow site is illustrated on Figs. 4,5 for  $\theta = 0 - 30^\circ$ . It is especially strong for BDT on the top site. The majority of the results is given for  $\theta = 10^\circ$ , which seems to be a reasonable choice for experimental SAMs. Note that in the upright position  $\theta = 0$  in top site (i.e. perpendicular to the contact surface, as was assumed in Ref. [18]) the overlap between the S  $x$  and  $y$  p-orbitals ( $xy$  being in contact surface plane,  $z$  normal to the contact) and the s-orbital on Au (or jellium) is *exactly zero* by symmetry, since  $\langle x|H|s \rangle = \langle y|H|s \rangle \equiv 0$ , where  $H$  is the Hamiltonian.

The s-electron on the top Au can only hop onto a S  $z$ -orbital via a  $\langle z|H|z \rangle = ss\sigma$  hopping integral. Obviously, for BDT on the top site, this result holds for all incident electrons with any  $\mathbf{k}_{\parallel}$ . Therefore, the  $x$  and  $y$  p-orbitals on S cannot be traversed by electrons incident from the contact. At the same time, only those states on the sulfur ion are coupled to conjugated  $\pi$ -orbitals on the benzene ring. Therefore, for the BDT on the top site and oriented normal to contact, the current will be *suppressed*, as observed in calculations by Di Ventra *et al.* [18,19]. Obviously, this symmetry selection rule is lifted for any  $\theta \neq 0$ . Thus, the previous calculations [18,19] have been performed at an artificial singular point. Incidentally, the same conclusion applies to the scattering of the carriers incident with  $\mathbf{k}_{\parallel} = 0$  (surface  $\Gamma$ -point) on upright BDT on a hollow site. Indeed, in this case the matrix element for hopping to the sulfur atom on the molecule is proportional to  $\sum_i \langle x_i|H|s \rangle \exp(i\mathbf{k}_{\parallel}\rho_i) \propto \sum_i l_i = 0$  for  $\mathbf{k}_{\parallel} = 0$ , where  $l_i$  are the directional cosines connecting the center of the triangle formed by three Au atoms on Au(111) surface with Au atoms in the corners at positions  $\rho_i$ . The same is obviously true of the hopping to the  $y$  p-orbital on S. Thus, in the case of BDT on a hollow site, *all* the contribution to the current comes from states with  $\mathbf{k}_{\parallel} \neq 0$ . Therefore, for BDT placed upright on the hollow site, the total current is *not* suppressed, as it is for BDT on the top site. Consequently, the current for BDT on the hollow site is considerably less sensitive to the precise contact geometry.

#### A. Density of states and transmission

Most of the present results can be appreciated from the analysis of the transmission probability  $T(E)$  and the density of states  $N(E)$  on the BDT molecule, see Figs. 2,3. One expects from the golden rule that the transmission would be proportional to the density of states. However, although peaks of both functions follow each other rather closely, there are important differences between the density of states and the transmission. It is easier to analyze the results for the top position first. There are two sharp peaks around the Fermi level  $E_F$ , marked as  $\pi^*$  (at  $E_{\pi^*} = E_F + 0.5$  eV) and  $\pi$  (at  $E_{\pi} = E_F - 1.0$  eV), Fig. 3(a). Transmission is almost zero at  $E > E_{\pi^*}$ , but there is a large density of *non-conducting* states in this energy interval. Those non-conducting states are formed at the end of the molecule and reside primarily on the end sulfur atom and gold atom on top of which the molecule sits, with little coupling to  $C\pi$  conducting states on the ring. The  $\pi^*$  peak contains mostly Au and S states and some  $C\pi$  ring states whereas the  $\pi$  peak is made mostly of S and  $C\pi$  ring states with a little addition of Au states. Sulfur atoms introduce the states in the HOMO-LUMO gap of the benzene ring (which is about 6.5 eV) and hybridize with

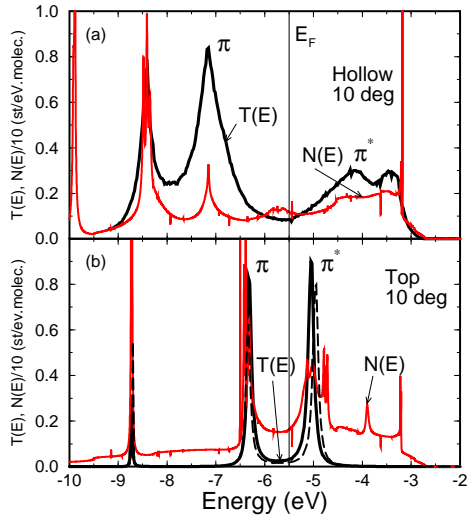


FIG. 2. Density of states  $N(E)$  and transmission  $T(E)$  through benzene-dithiolate (BDT) molecule on Au(111) as a function of energy: (a) BDT on the hollow site, (b) BDT on the top site (see text for the description of the configuration). The broken line indicates the transmission  $T(E)$  under the bias voltage 2V. Molecules in both configuration are tilted by  $10^\circ$ .

$C\pi$  states to make the conducting pathways across the BDT molecule. As a result, we see a much smaller gap between  $\pi$  and  $\pi^*$  states in BDT, which is  $E_{\pi^*} - E_{\pi} = 1.2$  eV. In the case of the hollow-site position, the situation is considerably different. There the  $\pi$  and  $\pi^*$  states are much broader and pushed apart by much stronger hybridization with three underlying Au atoms than for the top site, Fig. 3(b). The “soft” energy gap for the hollow position is  $E_{\pi^*} - E_{\pi} = 3.25$  eV, Fig. 3 (a) (cf. [20]).

It is instructive to compare the present results with the recent data for Ni-BDT-Ni SAMs [21] and jellium-LDA calculations [18]. The systems should have many similarities since Au and Ni have almost the same work function of about 5.1 eV [22]. In both systems a large conductance peak is observed at a bias of about  $V = 2.1$  V, which is larger than the earlier value of 1.4V [8]. The peak in Ni system is narrower and does not show any appreciable spin splitting. Interestingly, in Ni-BDT-Ni the additional resonant-like features are found at low bias voltages of about 0.3 V and 0.9 V. They correspond to smaller conductance compared to the peak at 2.1V. The position of the peaks should be compared with that of Ni d-states. It is well known that the energy of a minority peak in Ni DOS is very close to the Fermi level, whereas the majority peak is about 0.5eV below  $E_F$ . If the conducting molecular states were considerably smeared out, like in the case of hollow position, Fig. 2, then the observed low-bias features might be due to those peaks in Ni d-DOS. The fact that the first peak is observed at 0.3V, and not much smaller bias, may be due to energy dependence of the molecular density of “tail” states at  $E_F$ ,

which shifts the peaks by 0.3V. If, on the other hand, the peaks in the molecular density of states are sharp, like in the case of top position, Fig. 2, then the peaks in conductance should correlate with the position of the molecular orbital closest to the Fermi level (LUMO, according to the present work). The position of the LUMO in BDT in the present model is about 0.5 eV above the Fermi level for the top position. Therefore, we expect that in the top-site configuration there should be two peaks in the conductance, one at about 0.5-1.0 V (the position of the d-peak in Ni DOS with respect to the  $\pi^*$  resonance, depending on the connection between the molecule and the electrodes) and another at about 0.5 V higher than the first one (at 1.0-1.5 V). Interestingly, this is very similar to what was observed experimentally for the Ni-BDT-Ni system, with the peaks at  $V = 0.3$  V and 0.9 V [21]. If, on the other hand, the LUMO ( $\pi^*$  state) is at 1eV above the Fermi level, than the spin-peaks in Ni d-DOS might have produced the peaks in conductance at 2-3V. Indeed, there is a conductance peak at 2.1V in both Ni- and Au-based systems, but it is not spin-split in the case of Ni electrodes. It is worth mentioning that the position of the first peak in conductance is a strong function of the tilt angle, and it may vary significantly, Fig. 4. Finally, we note that the HOMO-LUMO gap in the “jellium” calculations is  $\sim 5$  eV [18], which is substantially larger than that in bare BDT molecules, and that is unlikely. The calculated value of the first peak in conductance in jellium-LDA is 2.4V, larger than the observed value of 2.1V. This suggests that the calculated gap is *larger* than the measured one, which is *contrary* to the usual notion that the LDA gaps are smaller than the experimental ones due to insufficient account of electron-electron correlations. As follows from this discussion, one needs more analysis to draw definitive conclusions about the position of the lowest conducting orbital with respect to the Fermi level in electrodes in Au-BDT-Au and Ni-BDT-Ni.

## B. Gating the molecules

The *gating effect* on the transmission and I-V characteristics is illustrated in Figs. 4,5. The gating is modeled by shifting the on-site energies on the molecule by  $\Phi_g$ , which is usually  $-0.5$ ,  $0$ , and  $0.5$  eV in the calculations. Obviously, in the experimental situation [7] such a large shift would require very large gating fields, comparable to the atomic fields in the order of magnitude. This is because one has to substantially change the electronic states on the molecule, and the characteristic energy is given by the HOMO-LUMO gap, usually a few electronvolts. Such large fields could not be possibly produced in the slot geometry with the channel length of only  $t = 1-2$  nm through the gate oxide with thickness  $L = 4-5$  nm [7]. Schematic of this gate is shown in inset in Fig. 4(a).

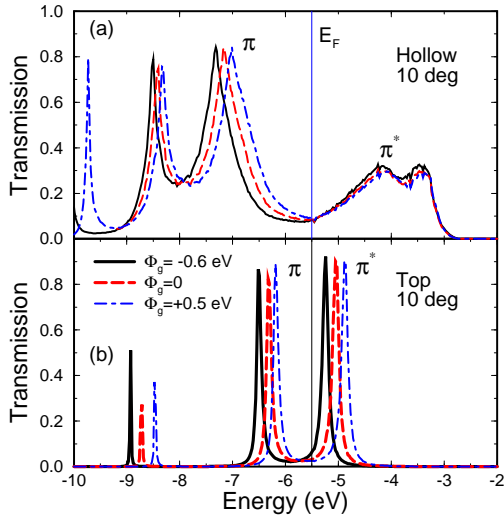


FIG. 3. Transmission  $T(E)$  through the BDT molecule on Au(111) and the effect of gating: (a) hollow site, (b) top site. The gating is simulated by shifting the on-site energies on BDT by  $\Phi_g = 0.5, 0$ , and  $-0.5$  eV. Note the presence of a sharp peak in  $T(E)$  for top site (originating from the LUMO on BDT) close to the Fermi level  $E_F$ .

The analytical solution to this electrostatic problem can be found by standard methods and it naturally contains a small parameter  $t/L \ll 1$ , so the gating on the molecule itself would be much smaller than the nominal gating voltage  $V_g$ .

One can speculate that large gating may result from e.g. charge accumulation in the gate oxide next to the molecular film. However, changing the oxide from  $\text{SiO}_2$  to  $\text{Al}_2\text{O}_3$  apparently has not modified the results [7]. Besides, there is an abrupt change of conductance by about an order of magnitude at the gate voltage  $V_g = -0.3$  V, which would suggest a high sensitivity of the interface charge to the bias voltage. Both facts are difficult to reconcile with the idea of interface charge accumulation but we will study this possibility.

Comparing Figs. 4(a) and 5(b), one observes that the smaller hybridization between S p- and Au s-states for BDT on the top site produces sharp features in the energy dependence of the transmission at the Fermi level. The LUMO in this case is above the Fermi level by only about 0.5 eV. The shifts of on-site energy by similar amount substantially change the transmission at the Fermi level, Fig. 4(a), and the corresponding current per molecule as shown in Fig. 5(a). There is a pseudogap at low voltages  $V \lesssim 1$  V, with the threshold voltage moving by an amount comparable to the external shift  $\Phi_g$  for the top-site configuration. By contrast, the large hybridization of S p-states with Au on the hollow site results in much broader energy tails of the resonant peaks in the density of states in the gap region in the vicinity of the Fermi level. Consequently, gating effect on the transmission, Fig. 5(b), and current, Fig. 5(b), is smaller compared to

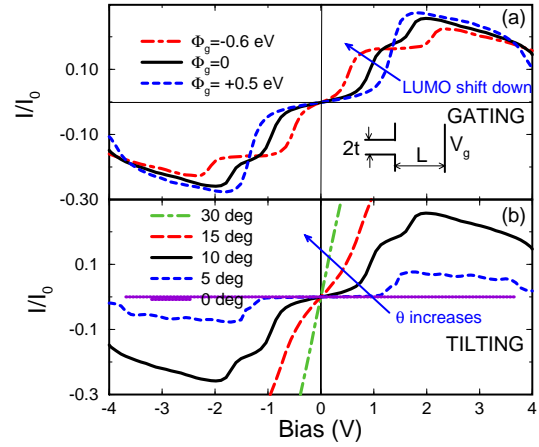


FIG. 4. Current-voltage characteristic and effects of gating and tilting with respect to the Au(111) electrode surface on current through the BDT molecule on the top site: (a) effect of the gating, onsite energies are shifted by the amount  $\Phi_g$  indicated on the figure, (b) effect of increasing tilt angle  $\theta$ . Current is in units of  $I_0 = 77.5 \mu\text{A}$ . Inset: schematic of the gate geometry,  $2t = 1$  nm,  $L = 4 - 5$  nm (nominal oxide thickness was 30 nm),  $V_g$  is the gate voltage.

the top-site situation.

For the hollow-site configuration there is no trace of the HOMO-LUMO gap in the I-V curve, and the I-V curve is almost *ohmic* in the wide range of voltages  $V < 2$  V (Fig. 5). This is indicative of the *metalization* of the chemically bonded molecule. This should have general implications, the simplest being an obvious difficulty in gating such molecules. This relates well to the large observed values of conductance (close to a conductance quantum) through a single molecule, and its small temperature dependence [23].

Finally, it is important to mention that in the present as well as other calculations, the LUMO is the closest molecular orbital to the Fermi level  $E_F$  and the maximum gating effect is naturally expected when its energy is pulled down closer to  $E_F$ . This takes place at *positive* gating voltage, and not the negative one, as observed experimentally [7]. This is an apparent contradiction which needs to be resolved.

### C. Effect of contact geometry

The tilting angle has a large effect on the I-V curves of BDT molecules, see Figs. 4, 5. The behavior of the BDT on the top site and on the hollow site is again rather different. The I-V curve for the hollow site remains ohmic for tilting angles up to  $75^\circ$  with moderate changes of conductance, Fig. 5(b). The variation of the current with the angle  $\theta$  are much larger for the top site, Fig. 5(a). By changing  $\theta$  from  $5^\circ$  to just  $15^\circ$ , one drives the I-V characteristic from one with a gap of about 2 V to the ohmic one with a large relative change of conductance.



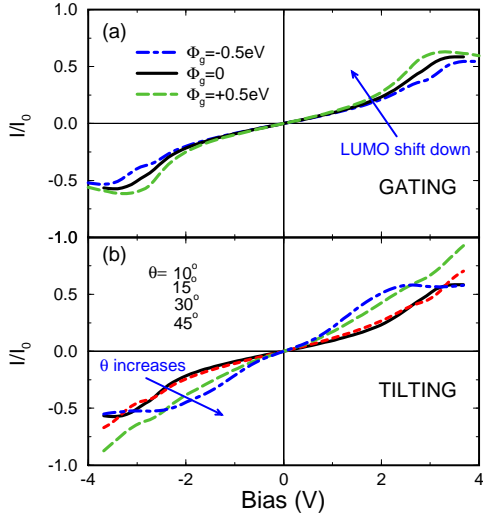


FIG. 5. Current-voltage characteristic and effects of gating and tilting with respect to the Au(111) electrode surface on current through the BDT molecule on the hollow site: (a) effect of the gating, (b) effect of increasing tilt angle. Current is in units of  $I_0 = 77.5 \mu A$ .

Even changing  $\theta$  from  $10^\circ$  to  $15^\circ$  changes the conductance by about an order of magnitude.

Finally, Fig. 6 illustrates the role of the electronic structure of the electrodes. The results described above have been obtained with only the s-states on Au atoms. We have also considered an sp- and spd-basis for Au. Although substantially increases the computing time, but the addition of p- and d-states brings about only moderate changes in current. Since the hybridization is different for different cases, the current magnitude slightly varies for different basis sets.

#### D. Possible origins of the observed gating effect

With regards to the origin of the observed gating effect, one can envisage that in dilute BDT-alkane solution sandwiched between Au electrodes there may be two processes going on that significantly change conductance. Since the BDT molecules are clamped by the matrix of alkane chains, they have to move with it. Note that the matrix of alkane chains is not in registry with the Au electrode. The BDT molecules have a nominal length of  $7.2 \text{ \AA}$  and are dissolved in the matrix of  $(\text{CH}_2)_5\text{S}$  alkanethiol insulating molecules with a nominal length of  $8.3 \text{ \AA}$ . Thus, the BDT molecule would appear as a dip on the surface of the matrix, and one or a few gold atoms can get into this dip during the deposition and bind to the end S. The geometry of this bond is uncertain, and the bond may well be stretched. In this case even a slight perturbation exerted on the SAM might lead to reconfiguration of the bond resulting in large changes of conductance. It seems reasonable to assume that the “domain

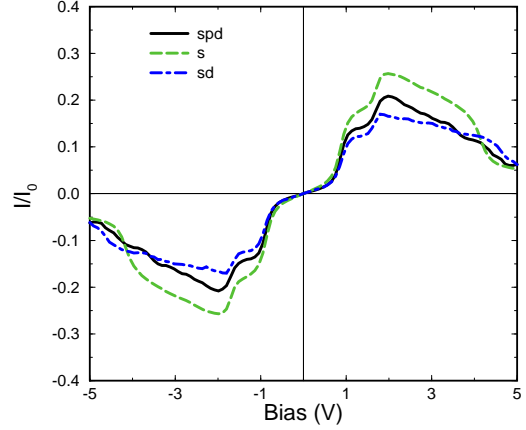


FIG. 6. Effect of electrode structure of Au(111) electrodes on current through the BDT molecule on the top site. There is moderate difference between calculations using s-, sp-, and full spd-bases. Current is in units of  $I_0 = 77.5 \mu A$ .

walls” separating different patches in an alkane matrix move rather freely in the system, since it does not require much energy. The BDT molecules will follow the matrix and can either snap from a hollow site to a top site and back and/or change the tilt angle. Both processes may be accompanied by large changes in the conductance. Conformational changes of the clamped BDT molecule are rather restricted, and the motion of the “domain walls” may be quite repeatable. One may wonder what causes the domain walls to move. As a possible reason, we suggest the presence of positive metal ions inside the organic film, as a small concentration of electrode ions in a SAM is rather inevitable. Indeed,  $\text{Au}^+$  strongly interacts with  $\text{C}_6\text{H}_6$  in the gas phase and forms an  $\text{Au}^+-\text{C}_6\text{H}_6$  complex with a binding energy 2.65 eV, whereas neutral Au forms a Van-der-Waals complex with the binding energy 90 meV [24]. Even more likely is a formation of those complexes with thiophenes, which carry an electric dipole. It is likely that a similar charged complex can form with BDT molecules in a SAM with those BDT molecules that have lost or are in poor contact with the gold substrate. It is also possible that a charged complex can be formed between the charged metallic ions ( $\text{Au}^+$  or other electrode metals) and alkane chains. A small field in the organic film will then produce a tangential force on the ions, and this may trigger the domain wall motion when the pinning is weak. Additionally, since the packing of the film is not ideal (an organic film is usually a rather disordered patchwork of “grains”), the Maxwell force acting on the top Au electrode at finite drain voltage and/or electron wind force may trigger the domain wall motion, which may also require a combination of these factors. The second possibility would be a build-up of the interface charge, but apparently the replacement of oxide did not change the results. As mentioned above, it

is also difficult to explain the jump in conductance at a certain value of the gate voltage.

#### IV. SUMMARY

We have presented an extensive analysis of the electronic states and transport through the benzenedithiolate molecule, which is the simplest conjugated molecule that forms a SAM and exhibits large changes of conductance under gating [7]. It shows that the effect of gating strongly depends on the geometry of the molecule-electrode contact, and is maximal for the less coordinated top-site position. It is related to the sharpness of the peak in transmission, which corresponds to the LUMO on BDT and is close to the Fermi level  $E_F$  of an Au electrode. By the same token, the current is more sensitive to the tilting angle of the molecule when it is positioned on the less coordinated top site. It is worth mentioning that the fact that the LUMO is closer to  $E_F$  suggests that a *positive* gating voltage  $V_g$  should produce the larger effect, not a negative gate voltage, as was observed in [7]. This discrepancy should be addressed in the future. Binding on the highly coordinated hollow site naturally leads to large hybridization of the molecular states with electrode states, which become smeared out. Consequently, BDT molecule becomes *metallized*, i.e. the I-V characteristic becomes practically ohmic. A very small effect of gating is predicted for this geometry. In any case, it is difficult to explain the large observed effect of gating on BDT molecules in a slot with a width of only 1 nm by small voltage applied to the gate 4-5 nm away. One should assume that there is either (i) a build-up of interface charge in the immediate vicinity of the slot opening, which is very sensitive to the gate voltage; or (ii) small inhomogeneous electrostatic forces and resulting stresses on the SAM result in the reconfiguration of the film and, consequently, of a clamped inside BDT molecule with respect to the gold contacts. Both of those mechanisms have problems of their own in explaining the experimental observations, as discussed in the text. Changes in random charges in the film and/or chemical composition of the BDT molecules (e.g. loss of end sulfur) are possible but are unlikely to be reversible. One needs to characterize the films better and vary the gate oxide thickness and other parameters of the system in order to confirm one of those mechanisms or suggest some other effects controlling the gating in slot geometries like the one used in Refs. [7,21].

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